

Abstract No. Graf0532

## **The Speciation of Arsenate (As (V)) at the Goethite-Water Interface in the Presence of Zinc (II)**

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Beamline(s): X11A

**Introduction:** The fate and bioavailability of both arsenic (As) and zinc (Zn) are of great environmental concern, due to their high toxicity and their carcinogenic properties in mammals. Arsenic contamination occurs frequently in areas where metal contamination (such as Zn) occurs simultaneously, e.g. around smelter areas, in acid mine drainage, in agricultural areas or in municipal wastes. We have been investigating the sorption behavior of As (V) at the goethite-water interface in the presence of Zn cations as a function of pH and initial As (V) and Zn (II) concentrations.

**Methods and Materials:** Arsenate and Zn(II) were reacted simultaneously in 2.5 g L<sup>-1</sup> suspensions of goethite at pH 4 and 7 with initial concentrations varying between 0.25mM and 2.5mM As (V) and Zn (II). The supersaturating limit in solution with respect to a zinc-arsenate precipitate is 0.30mM at pH 7. Suspensions receiving more than 0.25mM were titrated with As (V) and Zn (II) increments over an extended period of time such that solution concentrations would not exceed 0.25mM Zn (II) or As (V) at any point in time. EXAFS data were collected at the As (V) K-edge (11.874 keV).

**Results:** In the absence of Zn (II), arsenate forms bidentate binuclear complexes on the goethite surface at pH 4 and at pH 7 a monodentate mononuclear complex is observed. At pH 4 and 7, the presence of Zn significantly alters the speciation of As at the goethite-water interface by forming clusters with an As:Zn ratio of 1:3 to 1:4. These clusters become more abundant as the loading on the surface increases which becomes evident from decreasing disorders in the second shell and slight increases in the second shell coordination number. These clusters are however not the only As species present on the surface. Adsorbed bidentate binuclear species (pH 4, 0.25 and 2.5mM) and monodentate mononuclear species (pH 7, 0.25 and 0.75mM) can still be identified in fittings of As' second shell with iron (Fe) as an alternate second nearest neighbor.

Above 0.75mM As (V)/ Zn (II) at pH 7, As predominantly forms Zn-As clusters at the goethite-water interface. These clusters have a As: Zn coordination ratios in the second shell of 1:4 to 1:8, which indicates a transition from individual precipitate clusters to adamite like precipitates Zn<sub>2</sub>AsO<sub>4</sub>(OH) at the highest loading level. The disorder of these precipitates decreases with increasing surface loading.

**Conclusions:** The data suggest that As speciation in contaminated environments is strongly influenced by co-occurring metal cations, their concentration in solution, and the pH of the soil solution. Arsenate forms both direct adsorption complexes with the surface as well as recognizable Zn-As precipitates. The precipitated Zn-As phases are the dominantly recognizable form of As at high surface loadings. The existence of precipitate precursor A-type ternary complexes (Fe – O – Zn – O – As) could not yet be verified and require further examination. The solution chemistry of As and Zn is of great importance as heterogeneous nucleation reactions tend to be favored by soluble complexes. These type of data should be useful in formulating sound environmental remediation strategies.

**Acknowledgments** The authors are grateful for assistance from Kaumundi Pandya, X-11A beamline scientist at the NSLS, and the Environmental Soil Chemistry Group at the University of Delaware.

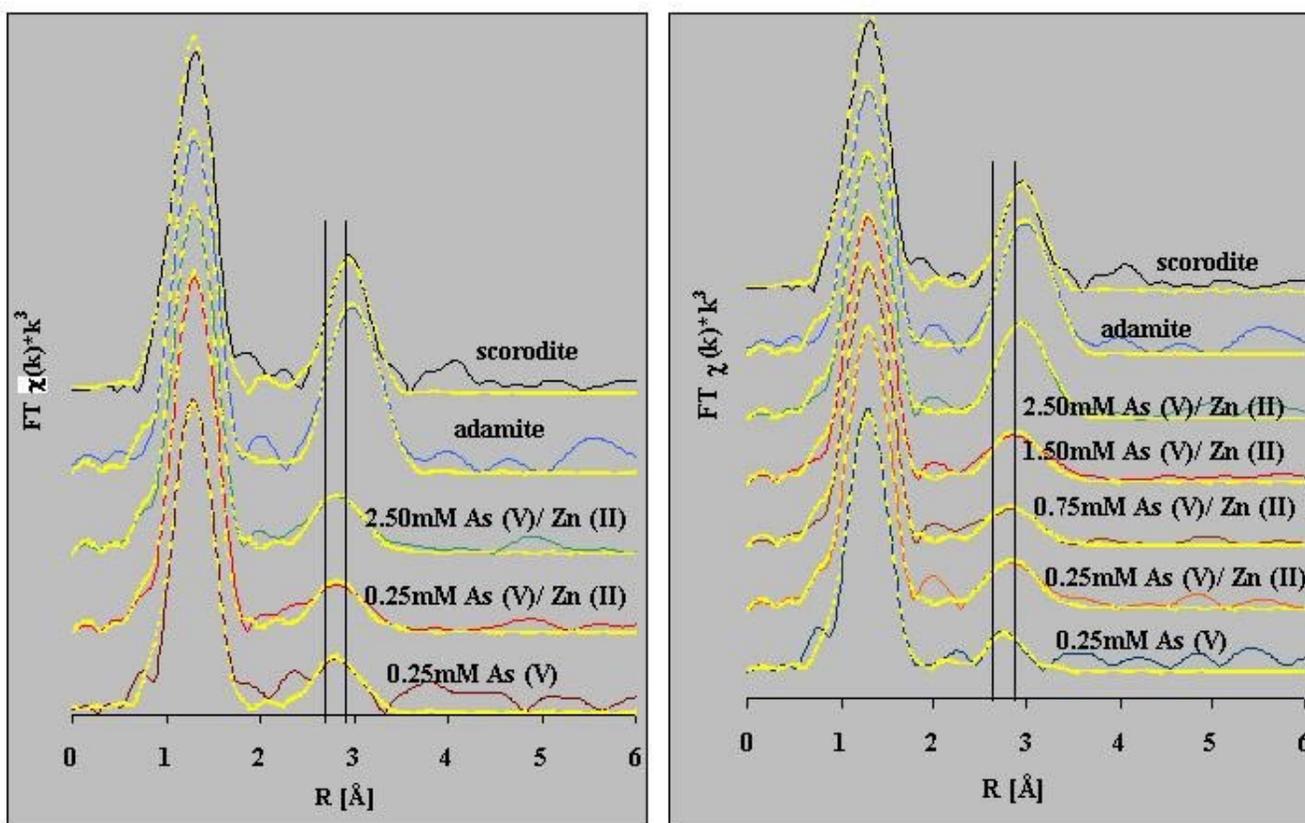


Figure 1: Left-Hand-Side) Fourier Transformed  $c(k) \cdot k^3$  weighted data of pH 4 As EXAFS samples; Right-Hand-Side) Fourier Transformed  $c(k) \cdot k^3$  weighted data of pH 7 As EXAFS samples. Solid lines represent the experimental data, yellow dotted lines represent the best fit.

Sample Name	pH	[concentration] <sub>0</sub> (mM)	Loading, $\Gamma$ [ $\sim \mu\text{mol m}^{-2}$ ]	As – O		As-Fe/Zn	
				CN $\pm 20\%$	R $\pm 0.03$	CN $\pm 30\%$	R $\pm 0.05$
As	4	0.25	1.43	5.62	1.69	2.90	3.25
As/Zn	4	0.75	1.41	6.26	1.70	3.28	3.36
As/Zn	4	2.50	4.16	5.72	1.70	3.73	3.34
As	7	0.25	1.01	5.79	1.69	1.65	3.34
As/Zn	7	0.25	1.08	6.21	1.70	1.38	3.34
As/Zn	7	0.25	1.08	5.46	1.70	2.53	3.35
As/Zn	7	0.75	3.77	5.81	1.70	3.12	3.36
As/Zn	7	1.50	7.80	5.67	1.70	4.17	3.38
As/Zn	7	2.50	13.20	5.03	1.69	7.51	3.34
Adamite			$\text{Zn}_2(\text{AsO}_4)(\text{OH})$	4.90	1.69	7.90	3.34
Scorodite			$\text{Fe}(\text{AsO}_4) \cdot 2\text{H}_2\text{O}$	5.96	1.68	4.52	3.35

Table 1: Structural parameters of As EXAFS data at pH 4 and 7. The Debye-Waller factor ( $\sigma^2$ ) was held constant in all samples except adamite and scorodite at 0.01.